

The University of Chicago

I. THE PREPARATION OF SOME METHYL TRIBORINE
TRIAMINES

II. THE PREPARATION AND PRELIMINARY STUDY
OF THE COMPOUND B_2H_7N

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1937

By
DAVID MOORE RITTER

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[Reprinted from the Journal of the American Chemical Society, 60, 1296 and 2297 (1938).]

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I. The Preparation of Some Methyl Triborine Triamines

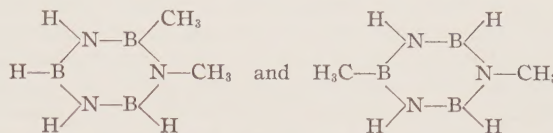
BY DAVID M. RITTER¹

Triborine triamine ($B_3N_3H_6$)² was first prepared by Stock and Pohland,³ who assigned to it the ring structure shown, on the basis of the evidence available at the time. The electron diffraction work of Stock and Wierl⁴ substantiated the ring structure. It was considered desirable, however, to test this structure further by a study of the methyl derivatives of the compound.

The preparation of derivatives in which methyl groups are attached to boron atoms of the ring, has been described by Schlesinger, Horvitz and Burg,² who found it possible to prepare three and only three such derivatives (by reactions of the methyl diboranes with ammonia), a result in agreement with the structure proposed by Stock and Pohland. The present work includes a parallel set of results: three and only three derivatives in which methyl groups are attached to the nitrogen atoms of the ring, resulted from the reaction of diborane with mixtures of ammonia and methylamine.

Although the work thus far described has led to the anticipated number of derivatives (for example, two and only two monomethyl triborine triamines, the B-methyl and the N-methyl), a final chemical proof of the ring structure must rest upon a study of the number of isomers resulting from replacement, by the same substituent, of hydrogen atoms attached to boron and hydrogen atoms attached to nitrogen. As a step in this direction, the action of boron trimethyl on mono-N-methyl triborine triamine has been studied. The reaction results in the formation of derivatives in which one, two, and three of the hydrogen atoms attached to boron are replaced by methyl groups, and, therefore, furnishes some of the desired derivatives, although in a roundabout, time-consuming fashion.

Of particular interest is the mono-N-methyl mono-B-methyl derivative. This should exist in two isomeric forms



The present method of preparation, by the action of boron trimethyl on mono-N-methyl triborine triamine, might be expected to yield a mixture of the two isomers. The material having this composition thus far, however, has given no indication of being a mixture; should it actually prove to be a pure substance, the fact would indicate a strong influence favoring substitution in the ortho rather than the para position, or *vice versa*. The indications arising from a study of the further substitution of the B-linked hydrogen atoms by methyl groups, are difficult to interpret; hence the question of such directive influences remains an interesting, though difficult, problem for further study.

In the course of this work, better conditions for the preparation of triborine triamine and its derivatives were found. These studies led also to the discovery of the new compound, B_2H_7N , whose preparation, properties, and structure are described in Part II.

Experimental Methods

Apparatus and Technique.—The apparatus and technical methods employed in this investigation are like those of Stock⁵ and of Schlesinger and Burg and their co-workers.⁵

Analytical Methods.—The analytical methods are substantially those employed in previous investigations of triborine triamine and its derivatives.^{2,3} In those analyses in which nitrogen was determined as the free element, the procedure of Stock and Pohland³ was modified in three details:

1. The combustion train was operated without the addition of oxygen gas.

2. A single combustion tube contained all of the substances required for the combustion and for the reduction of the oxides of nitrogen; it was packed with the materials required in the order: lead chromate, copper oxide, copper reduced from copper oxide, finely divided nickel.

3. The apparatus was arranged in the form of a circuit, including a small mercury vapor circulating pump by which any unburned vapors were fed back through the combustion tube, along with the nitrogen first produced. This system was checked before each determination, by the analysis of a sample of pure methylamine.

- (5) Stock, *Ber.*, **54A**, 142 (1921) and "Hydrides of Boron and Silicon," Cornell University Press, 1933, Chapter XXX; Schlesinger and Burg, *J. Am. Chem. Soc.*, **53**, 4321 (1931); Burg, *ibid.*, **56**, 499 (1934).

(1) The author wishes to acknowledge the aid extended him and interest shown during this investigation, by Dr. H. I. Schlesinger and Dr. Anton B. Burg.

(2) This compound was not named at the time of its discovery. The name used here was suggested by Schlesinger, Horvitz and Burg, *J. Am. Chem. Soc.*, **58**, 409 (1936).

(3) Stock and Pohland, *Ber.*, **59B**, 2215 (1926).

(4) Stock and Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931).

The N-methyl B-methyl triborine triamines were analyzed by the following procedure. The measured sample was condensed by means of liquid nitrogen in a tube containing an excess, measured quantity of standard hydrochloric acid. The tube was sealed off, heated in a steam-bath for several hours to ensure the complete hydrolysis of the sample, and again connected to the vacuum apparatus by means of the tube opener. The hydrogen resulting from hydrolysis was pumped through a trap and measured; the substances remaining in the tube and trap (at -196°) were warmed to room temperature and then washed into a flask. The excess of acid was titrated to the methyl red end-point, in order to determine the nitrogen as ammonia and methylamine (by difference); then mannite was added and the boric acid was titrated to the phenolphthalein end-point. In those analyses in which methylboric acid was produced by the hydrolysis, the determination of the total boron required that the solution be saturated with mannite.

Vapor Tensions.—The pressures of saturated vapor at different temperatures were determined in static systems. In cases of low volatility, the measurements were carried out at elevated temperatures by the aid of apparatus of the type designed for such purposes by Stock and Kusz.⁶

Gas Volumes.—All volumes, unless otherwise stated, are given in cubic centimeters of gas at 0° and 760 mm. pressure.

Molecular Weights.—The molecular weights of the various compounds were calculated from their vapor densities, determined at temperatures between 100 and 150° . The apparatus used for the measurements of volume was like that employed for vapor tensions at elevated temperatures, except that the small tube for containing the sample was replaced by a calibrated bulb large enough for the complete vaporization of the material. The agreement between the observed and calculated molecular weights was generally quite satisfactory, in view of the small sizes of the samples involved.

The Preparation of Triborine Triamine and Its N-Methyl Derivatives

The Effect of Pressure upon the Yields of Triborine Triamine.—In a search for the best preparative conditions, the effect of the total pressure developed in the reaction, upon the yield of triborine triamine, was studied. The pressures were calculated from the total quantities of gaseous products and the volumes of the bomb-tubes employed for the reaction. The results are given in Table I.

TABLE I

RELATION OF PRESSURE TO YIELD OF TRIBORINE TRIAMINE

Press. at 200° , atm.	1.8	4.1	4.8	11
Yield, %	27	33	38	41.5

These results show that the yields of triborine triamine may be improved somewhat over those reported by Stock and Pohland,³ by confining the reacting materials to a sufficiently small relative space. Incidentally, the observation of these authors, that a short period of heating (as brief as fifteen minutes) is sufficient for complete reaction, was confirmed.

(6) Stock and Kusz, *Ber.*, **47**, 3115 (1914).

Preparation of the N-Methyl Triborine Triamines.

The pyrolysis of samples obtained by mixing diborane, ammonia, and primary methylamine, yields triborine triamine and its N-methyl derivatives, in proportions depending upon the ratio of methylamine to ammonia. The general equation for the reactions involved is $3B_2H_6 + 2xCH_3NH_2 + 2(3 - x)NH_3 \rightarrow 2B_3N_3H_{6-x}(CH_3)_x + 12H_2$. If ammonia is absent ($x = 3$), only the tri-N-methyl derivative is produced.⁷ If the proportions of ammonia and methylamine correspond to $x = 1$, the principal product is the mono-N-methyl derivative, along with smaller quantities of the other compounds. When $x = 2$, however, there is obtained a mixture in which no one of the derivatives predominates; only triborine triamine itself appears in minor quantity.

For each of these experimental preparations, the reactants were measured as gases in the vacuum apparatus, and condensed one after the other into a bomb tube, which was next sealed off and immersed for fifteen to thirty minutes in an oil-bath at 200° .

The volatile reaction products were transferred from the bomb tube to the vacuum apparatus by means of the tube-opener, and the hydrogen was pumped off through a trap at -196° . The condensed products were separated by fractional condensation, through a series of U-tubes at -45° , -65° , -80° , -90° , and -196° , respectively. The first of these U-tubes held the tri-N-methyl triborine triamine; di-N-methyl triborine triamine was caught at -65° ; the mono-N-methyl derivative condensed at -80° , along with a trace of triborine triamine itself; the U-tube at -90° held most of the triborine triamine, while any residual ammonia, methylamine, or diborane passed into the last trap. Each condensate was purified by further fractionation.

Large samples (e. g., 50 cc. of gas) of the mono-N-methyl derivative were freed from triborine triamine by the aid of a very small fractionating column.⁸ This column was operated under high vacuum (without pressure head), with the reflux temperature at -78.5° , and the effluent gases were condensed directly in a trap at -196° . Under these conditions, a small part of the mono-N-methyl derivative was carried past the reflux tube, but was easily recovered and purified by fractional condensation.

It was observed that the yields of the triborine triamine nucleus from mixtures containing methylamine, were higher than those obtained from pure $B_2H_6 \cdot 2NH_3$. Thus when ammonia was absent, the yields (of N-trimethyl triborine triamine) ran above 60%.

The analytical data on which the characterization of the three N-methyl derivatives is based, are given in Table II. All values here given are expressed in millimoles.

The values for the molecular weights calculated from the experimentally determined vapor densities together with the values calculated from the formulas, are given in Table III.

(7) Incidental to such preparations was the preparation of the dimethylamine of diborane, $B_2H_6 \cdot 2CH_3NH_2$. Quite in contrast to the diammoniate of diborane, this compound is a liquid at room temperature, although it cannot be volatilized without complete change of identity. Like the diammoniate of diborane, it appears to be entirely stable at room temperature.

(8) Burg, *J. Am. Chem. Soc.*, **56**, 499 (1934).

TABLE II

ANALYTICAL DATA FOR THE N-METHYL TRIBORINE TRIAMINES

Compound	Substance determined	Size of sample	Calcd. quantity	Quantity found
N-CH ₃ B ₃ N ₃ H ₅	N ₂	0.119	0.179	0.178
	CO ₂	.151	.151	.153
	B(OH) ₃	.151	.453	.462
	H ₂	.139	.417	.415
N-(CH ₃) ₂ B ₃ N ₃ H ₄	N ₂	.0745	.112	.115
	H ₂	.223	.669	.684
N-(CH ₃) ₃ B ₃ N ₃ H ₃	N ₂	.108	.162	.155
	CO ₂	.120	.360	.368
	B(OH) ₃	.120	.360	.366
	H ₂	.162	.486	.469
	H ₂	.140	.420	.422

TABLE III

MOLECULAR WEIGHTS OF THE N-METHYL DERIVATIVES

Compound	Temp., of detn., °C.	Molecular weight	
		Obsd.	Calcd.
N-CH ₃ B ₃ N ₃ H ₅	101	94.7	94.5
N-(CH ₃) ₂ B ₃ N ₃ H ₄	158	109	108.5
N-(CH ₃) ₃ B ₃ N ₃ H ₃	123	123	122.5

The temperatures at which the sample volumes were measured are significant, because of the tendency of these substances to associate in the vapor phase at lower temperatures. This effect seems most pronounced in the case of the mono-N-methyl derivative. At room temperature, two observations of the vapor density of this substance gave average molecular weights of 117 and 129, respectively, in contrast to the calculated 94.5. An attempt to measure the effect of pressure upon the degree of association of this derivative was abandoned on account of the slowness with which the equilibrium was approached.

The vapor tensions of the three N-methyl derivatives of triborine triamine at different temperatures appear in Table IV, which gives also the corresponding temperatures, calculated from the equations of the type $\log p = B - A/T$. The constants for these equations, calculated by the method of least squares from the original data, appear in Table V, which gives also the calculated value of the boiling point, the molar heat of vaporization, and the Trouton constant, for each compound.

The B-Methyl Derivatives of N-Methyl Triborine Triamine

B-Methylation of Triborine Triamine.—The behavior of triborine triamine toward boron trimethyl and toward dimethylboric amide was

studied as a test of the feasibility of the direct B-methylation of the N-methyl derivatives of triborine triamine. Both reagents gave B-methyl derivatives, along with non-volatile solid by-products, hydrogen, and occasionally methane. Boron trimethyl gave better yields of the desired

TABLE IV

VAPOR TENSIONS OF THE N-METHYL DERIVATIVES

<i>P</i> _{mm.}	<i>T</i> _{obsd.}	<i>T</i> _{calcd.}	<i>P</i> _{mm.}	<i>T</i> _{obsd.}	<i>T</i> _{calcd.}
N-CH ₃ B ₃ N ₃ H ₅			N-(CH ₃) ₂ B ₃ N ₃ H ₄		
5.2	247.5	246.3	8.2	273.1	270.5
7.5	252.5	252.1	27.0	293.1	292.9
10.5	257.5	257.6	32.5	298.1	296.7
14.0	262.5	262.5	59.5	309.6	309.9
18.8	267.5	267.8	84.5	317.1	318.1
23.5	273.1	271.9	99.5	322.1	322.1
32.7	278.2	278.2	111.0	323.6	324.8
41.5	282.5	283.0	152.5	331.6	332.9
52.0	287.5	286.5	204	338.6	340.7
N-(CH ₃) ₃ B ₃ N ₃ H ₃			225	341.6	343.5
96	345.1	344.6	302	350.3	351.9
157	358.1	357.7	360	358.7	357.1
271	372.6	373.4	402	360.1	360.5
299	376.6	376.4	496	366.0	367.1
376	382.7	383.6	530	368.9	369.2
429	388.1	388.8	611	374.0	373.9
610	399.1	399.6	754	382.6	381.0
754	407.1	407.1			

TABLE V

PHYSICAL CONSTANTS FROM THE VAPOR TENSIONS

Compound	A	B	B. p., °C.	Δ <i>H</i> , cal./mole	Trouton constant
N-CH ₃ B ₃ N ₃ H ₅	1713	7.669	84	7975	22.3
N-(CH ₃) ₂ B ₃ N ₃ H ₄	1832	7.685	108	8375	21.9
N-(CH ₃) ₃ B ₃ N ₃ H ₃	2009	7.812	134	9278	22.7

TABLE VI

THE ACTION OF BORON TRIMETHYL UPON TRIBORINE TRIAMINE

Experiment	1	2	3	
Reactants $\left\{ \begin{array}{l} \text{B}_3\text{N}_3\text{H}_6, \text{ cc.} \\ \text{B}(\text{CH}_3)_3 \end{array} \right.$	8.7 6.9	7.9 7.8	14.8 5.0	
Temperature, °C.	200-225	100	100	
Duration of heating, hrs.	1.75	24	6	
Products $\left\{ \begin{array}{l} \text{H}_2, \text{ cc.} \\ \text{CH}_4, \text{ cc.} \\ \text{B-CH}_3\text{B}_2\text{N}_3\text{H}_5, \text{ cc.} \\ \text{B-(CH}_3)_2\text{B}_2\text{N}_3\text{H}_4, \text{ cc.} \\ \text{B-(CH}_3)_3\text{B}_2\text{N}_3\text{H}_3, \text{ cc.} \\ \text{B}_2\text{H}_6, \text{ B(CH}_3)_3, \text{ and} \\ \text{their reaction prod-} \\ \text{ucts, cc.} \\ \text{Recovered B}_3\text{N}_3\text{H}_6, \text{ cc.} \end{array} \right.$	10.6 2.0 0.6 0.86 1.5 0.0 0.0	4.6 0.0 0.4 4.6 3.8 0.0	1.6 0.0 0.14 0.96 1.5 3.6 9.1	
	Recovery of triborine triamine nucleus, %	34	63	79
	Yield of substituted ring-compounds, %	34	63	46

TABLE VII
THE ACTION OF BORON TRIMETHYL UPON N-METHYL TRIBORINE TRIAMINE

Experiment	1	2	3	4	5	Totals
Reactants and Conditions:						
N-CH ₃ B ₃ N ₃ H ₅ , cc.	10.1	8.25	17.5	30.0	6.25	72.1
B(CH ₃) ₃ , cc.	9.6	7.8	6.0	30.3	6.54	60.2
Pressure, atm.	1.1	1.0	1.3	3.3	0.15	—
Time, hours	6	48	30	12	12	—
Temperature, °C.	100	100	100	100	100	—
Products:						
H ₂ (possibly with CH ₄), cc.	Trace	1.94	6.0	1.2	0.06	9.3
N-B-(CH ₃) ₂ B ₃ N ₃ H ₄ , cc.	1.8	1.1	3.1	Trace	—	6.5
N-B,B'-(CH ₃) ₃ B ₃ N ₃ H ₃ , cc.	←	present	→	→	0.43	15.5
N-B,B',B''-(CH ₃) ₄ B ₃ N ₃ H ₂ , cc.	←	present	→	→	→	4.6

TABLE VIII
ANALYTICAL DATA FOR THE N-B-METHYL DERIVATIVES

Compound	Size of sample	H ₂		NH ₃ and CH ₃ NH ₃		Boric acids	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
N-B-(CH ₃) ₂ B ₃ N ₃ H ₄	0.071	0.143	0.142	0.208	0.213	0.209	0.213
	.053	.107	.106	—	—	—	—
N-B,B'-(CH ₃) ₃ B ₃ N ₃ H ₃	.118	.116	.118	—	—	—	—
N-B,B',B''-(CH ₃) ₄ B ₃ N ₃ H ₂	.199	.000	.000	0.591	0.596	0.592	0.596

products; the results of experiments with this reagent are given in Table VI.

B-Methylation of Mono-N-methyl Triborine Triamine.—The action of boron trimethyl on mono-N-methyl triborine triamine is similar to its action on triborine triamine itself. Three N-B-methyl derivatives were prepared by that method: mono-N-methyl mono-B-methyl triborine triamine, mono-N-methyl di-B-methyl triborine triamine, and mono-N-methyl tri-B-methyl triborine triamine. The data are listed in Table VII. This table does not give the yields of tri- and tetramethyl derivatives from each separate experiment, for the task of isolating these from each mixture was considered unprofitably cumbersome.

The method of purification of each of the two lighter N-B-methyl derivatives was the same as that used for the isomeric N-methyl derivative. Mono-N-methyl tri-B-methyl triborine triamine was purified by condensing it several times in a U-tube at -30° , while the more volatile substances passed through.

The analytical data upon which the characterization of the N-B-methyl derivatives is based, are listed in Table VIII. The quantities are given in millimoles.

The molecular weights found, together with the values calculated from the formulas, are given in Table IX.

TABLE IX
MOLECULAR WEIGHTS OF THE N-B-METHYL DERIVATIVES

Compound	Value found	Value calculated
N-B-(CH ₃) ₂ B ₃ N ₃ H ₄	109	108.4
N-B,B'-(CH ₃) ₃ B ₃ N ₃ H ₃	123.6	122.4
N-B,B',B''-(CH ₃) ₄ B ₃ N ₃ H ₂	138	136.4

The vapor tensions of the three B-methyl derivatives of N-methyl triborine triamine at different temperatures appear in Table X, which gives also the corresponding temperature values calculated from the equations of the type $\log p = B - A/T$. The constants for these equations,

TABLE X
VAPOR TENSIONS OF THE B-METHYL DERIVATIVES OF N-CH₃B₃N₃H₅

N-B-(CH ₃) ₂ B ₃ N ₃ H ₄			N-B,B'-(CH ₃) ₃ B ₃ N ₃ H ₃		
P _{mm.}	T _{obsd.}	T _{calcd.}	P _{mm.}	T _{obsd.}	T _{calcd.}
4.2	261.9	261.5	43.0	326.1	326.4
5.7	266.9	266.9	61.5	336.1	335.1
7.4	271.9	271.6	73.0	338.6	339.4
9.5	276.9	276.3	98.3	347.6	347.1
12.7	281.9	282.0	118.5	352.1	352.2
16.9	286.9	287.8	151.0	358.6	359.0
22.0	291.9	293.4	178.2	363.6	363.8
N-B,B',B''-(CH ₃) ₄ B ₃ N ₃ H ₂	201.3	368.1	201.3	368.1	367.4
	241.0	372.6	241.0	372.6	372.8
	27.8	339			
	84	365			
	112	373			
	153	380			
	268	397			

calculated from the original data by the method of least squares, appear in Table XI, along with the calculated boiling points, molar heats of vaporization, and Trouton constants.

TABLE XI

PHYSICAL CONSTANTS FROM THE VAPOR TENSIONS

Compound	A	B	B, p., °C.	H, cal./mole	Trouton constant
N-B-(CH ₃) ₂ B ₃ N ₃ H ₄	1732	7.245	124	8013	20.2
N-B,B'-(CH ₃) ₃ - B ₃ N ₃ H ₃	1965	7.652	139	8916	21.6
N-B,B',B''-(CH ₃) ₄ - B ₃ N ₃ H ₂	2294	8.207	158	10440	24.2

Summary

The mono-, di-, and tri-N-methyl derivatives of triborine triamine were prepared by brief heating of mixtures of diborane, ammonia, and methylamine. The mono-, di-, and tri-B-methyl derivatives of mono-N-methyl triborine triamine were prepared by heating the parent substance with boron trimethyl. The uniformity of each sample was confirmed by the agreement of the vapor tensions with the Clapeyron-Clausius equation. The production of these six derivatives, and no others, is a confirmation of the ring structure for triborine triamine.

II. The Preparation and Preliminary Study of the New Compound B₂H₇N

By DAVID M. RITTER,¹

In the preparation of triborine triamine (B₃N₃H₆) from ammonia and diborane, small quantities of a new volatile compound having the molecular formula B₂H₇N were obtained.² The formation of this compound, for which the structural formula $\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & \diagdown & / \\ \text{B} & \text{---} & \text{N} & \text{---} & \text{B} \\ & / & \diagdown \\ \text{H} & \text{H} & \text{H} \end{array}$ seems most appropriate, is an

important part of the evidence in favor of the hypothesis that many of the reactions of diborane are caused by its dissociation into unsaturated borine ($\begin{array}{c} \text{H} \\ | \\ \text{H} : \text{B} : \text{H} \end{array}$) molecules.³ It is, therefore, of interest to describe the preparation and properties of the new compound, as well as to present further evidence concerning its structure.

Preparation.—The observation that B₂H₇N was obtained only when diborane was used in excess of that required by the formula B₂H₆·2NH₃, suggested that it is formed by the action of diborane upon the "diammoniate,"⁴ rather than by the direct reaction of diborane with ammonia. It therefore seemed likely that the yield of B₂H₇N would be improved considerably if diborane were passed over the "diammoniate," under conditions subject to close control.

The apparatus used for this flow method was the one which had been employed before, in the preparation of B₄H₁₀ and B₃H₁₁.⁵ Ammonia was condensed as a thin layer upon the walls of the first U-tube (U4A in the article referred to above) and converted to the "diammoniate" by exposing it to an excess of diborane while the tube was warmed slowly from -130° to room temperature.⁶ Then a large sample of diborane was condensed in the graduated tube M, and allowed to evaporate at -80°; the gas passed through the U-tube containing the ammoniate, at a rate limited by the capillary tube C. All condensable gases and vapors were trapped in the second U-tube (at -195°), while the hydrogen passed through and registered its pressure upon a manometer in the main vacuum apparatus beyond. The proper temperature for the first U-tube was determined by warming that U-tube until the movement

of the mercury in the manometer indicated a satisfactory rate of reaction.⁷ After the evaporation of the last of the diborane, the major part was recovered from the material trapped in the second U-tube; in most cases it was passed through the system again, until no important quantities of hydrogen were evolved in the process. The conditions and results of four such experiments are given in Table I.

TABLE I

FLOW METHOD OF PREPARING B₂H₇N

Ammonia, cc. ^a	Total B ₂ H ₆ , cc.	No. of passages	Flow rate, cc./min.	Temp., °C.	Diborane destroyed, cc.	B ₂ H ₇ N formed, cc.	% yield (based on diborane)
105	422	1	10	100	75	14.7	19
120	730	1	5	85	83	25.0	30
173	613	2	12	85	100	29.0	29
142	877	2	30	88	108	36.0	33

^a All gas volumes in this paper refer to standard conditions.

The product was purified by fractional condensation: it passed through a U-tube at -55°, and condensed completely at -80°.

Analysis and Molecular Weight.—Measured samples of the vapor were treated with known volumes of standard hydrochloric acid in sealed tubes. The resulting hydrolyses were completed in ten minutes at room temperature.⁸ The hydrogen was collected for measurement over mercury by means of a Töpler pump with a trap at -196°; the contents of the trap and of the hydrolysis tube were then washed into a flask. The excess acid was titrated to the methyl red end-point; the difference between the quantity of acid originally used and that found by this titration represents ammonia nitrogen. Subsequent titra-

TABLE II

ANALYTICAL DATA FOR B₂H₇N

Sample	Hydrogen		Boric acid		Ammonia	
	Quantity	Ratio	Quantity	Ratio	Quantity	Ratio
0.0846	0.418	4.94 ^a	0.167	1.97	..	..
.0589	..	..	..	..	0.0587	1.00
.428	..	..	..	..	.406	0.95
.196	.985	5.02	..	..	..	..
.166	.848	5.10	..	..	..	..
.303	..	..	.594	1.96	..	..

^a In this case, the sample was heated for five hours at 100° with water containing no acid.

(7) It is important to employ the lowest feasible temperature, because higher temperatures lead to frothing, with the danger of clogging the capillary, and also facilitate the formation of traces of such impurities as B₄H₁₀, B₃H₁₁, and B₃N₃H₆.

(8) When pure water was used, the hydrolysis was far more difficult, probably because the free ammonia first liberated acted as a base to hinder the hydrolysis of the B-H links. Thus a sample which was left in contact with water in a sealed tube for two months at room temperature produced only 3.8 of the expected 5 volumes of hydrogen.

(1) The author wishes to express his thanks to the Research Corporation for providing funds for the liquid nitrogen used in a large portion of the work described in this and in the first part of this dissertation.

(2) Cf. Part I of this dissertation.

(3) Other evidence on this subject appears in two earlier papers: Burg and Schlesinger, *ibid.*, **59**, 780 (1937); Schlesinger and Burg, *ibid.*, **60**, 290 (1938).

(4) For the structure of this compound, see Schlesinger and Burg, *ibid.*, **60**, 290 (1938).

(5) Burg and Schlesinger, *ibid.*, **55**, 4012 (1933).

(6) The preparation of the diammoniate by the slightly more tedious process of carrying on the reaction at -120° and removing the residual ammonia at -80°, led to no change of yield.

TABLE III
 CORRECTED VAPOR PRESSURES OF B_2H_7N

t°	-27.2	-23.0	-16.2	-13.4	-9.6	-3.6	0.00	3.8
$p_{mm.}$, obsd.	5.3	7.65	12.0	14.6	18.9	26.1	32.3	39.3
$p_{mm.}$, calcd.	5.7	7.64	12.1	14.4	18.3	26.3	32.3	39.8
t°	7.9	11.0	15.4	20.0	22.6	25.4	27.3	28.9
$p_{mm.}$, obsd.	49.6	57.8	72.5	90.3	102.0	117.0	126.8	135.9
$p_{mm.}$, calcd.	49.6	58.4	72.6	90.8	102.5	116.7	126.8	136.2

tion of the solution to the phenolphthalein end-point in the presence of an adequate quantity of mannite gave the amount of boric acid present. The results are given (in millimoles) in Table II.

These results agree with the formula B_2H_7N , as shown by the equation $B_2H_7N + 4H_2O + H^+ \longrightarrow 2HBO_2 + NH_4^+ + 5H_2$.

The molecular weight calculated from the observed vapor density also agreed with the formula B_2H_7N (obsd. 42.9 and 42.2; calcd. 42.6).

The melting point was determined by observations on two separately purified samples. The values, taken by means of an ammonia vapor pressure thermometer, were -66.5 and -66.4° .

The vapor pressure at various temperatures determined the equation

$$\log_{10} p_{mm.} = -(2097/T) + 1.75 \log_{10} T - 0.00642T + 6.677$$

From this equation, the molar heat of vaporization is estimated as 7300 cal., and the Trouton constant as 21.0 cal./degree mole. The normal boiling point is calculated to be 76.2° .

Decomposition and Thermal Stability.—The substance B_2H_7N can be kept for several days at room temperature without appreciable decomposition, but a sample which had been held for six hours at 45° showed an increase of vapor pressure, corresponding to about 0.2 cc. of diborane (from a 5-cc. sample). A sample left for sixteen months in a sealed bulb at room temperature, decomposed almost completely, evidently according to the equation $2B_2H_7N \longrightarrow B_2H_6 + (BH_4N)_x$; the actual results were complicated by secondary production of hydrogen, and by the probable presence of $B_3N_3H_6$ in the original sample.⁹

The 5.6-cc. sample yielded 2.4 cc. of diborane, 0.6 cc. of hydrogen, and 0.4 cc. of material having approximately the volatility of $B_3N_3H_6$. The diborane was fully identified by its vapor pressure (226 mm. at -112°) and by hydrolysis, which yielded 14.4 cc. (6.1 volumes) of hydrogen and 0.214 millimole of boric acid (2.00 equivalents per mole). The non-volatile solid was not investigated further.

The Behavior of B_2H_7N toward Trimethylamine.—A stable addition product $(CH_3)_3-$

$N \cdot B_2H_7N$, is produced by the action of trimethylamine upon B_2H_7N at -80° . Heating this product with excess trimethylamine results in the removal of a BH_3 group to produce one molecule of borine trimethylamine per mole of B_2H_7N originally used.

Thus 2.7 cc. of B_2H_7N , treated with 12.2 cc. of trimethylamine at -80° , absorbed 2.8 cc. of the latter, to give a white solid which failed to react further during two hours at room temperature. During three hours at 100° , however, there resulted 2.80 cc. of material whose vapor pressures were measured as 18.6 mm. at 69.5° and 10.6 mm. at 59.8° , in good agreement with the data recorded earlier for borine trimethylamine.¹⁰ There resulted also 2.9 cc. of hydrogen, and a further 0.9 cc. of trimethylamine was used up. A trace (0.3 cc.) of material which seemed to be $B_3N_3H_6$, also was found among the products. The residual solid thus seemed to have the composition $BNH_2^{1/2}N(CH_3)_3$.

The Behavior of B_2H_7N toward Ammonia.—

Like trimethylamine, ammonia adds to B_2H_7N to give a stable solid mono-ammoniate, $B_2H_7N \cdot NH_3$. By the sudden heating of this substance to 200° , a 45% yield of $B_3N_3H_6$ is obtained; this yield is somewhat higher than that obtained directly from the "diammoniate of diborane."

In a typical experiment, 5.2 cc. of B_2H_7N and 17.7 cc. of ammonia were left together for one hour at -80° . Then the excess ammonia was distilled to another part of the vacuum apparatus, while the reaction tube was being warmed to room temperature. The removed ammonia was measured as 12.6 cc., indicating that the white solid residue contained 5.1 cc. of combined ammonia. Five minutes of heating of the product at 50° caused the evolution of only 0.25 cc. of volatile material.

Another sample of the solid, composed of 9.65 cc. of B_2H_7N and 9.65 cc. of ammonia, was allowed to stand for two months at room temperature ($25-30^\circ$): it produced 0.3 cc. of hydrogen and an even smaller trace of material which was trapped at -196° .

A sample composed of 4.8 cc. of B_2H_7N and 4.9 cc. of ammonia was heated for five minutes in a sealed tube at 200° . The products were 15.1 cc. of hydrogen, 1.4 cc. of $B_3N_3H_6$, 0.26 cc. of an unidentified substance slightly more volatile than $B_3N_3H_6$, and non-volatile solids. The yield of $B_3N_3H_6$ thus was slightly less than 45%.

The Behavior of $B_2H_7N \cdot NH_3$ toward Sodium in Liquid Ammonia.—When the compound $B_2H_7N \cdot NH_3$ is dissolved in liquid ammonia and

(9) This particular sample had been obtained as a by-product in the preparation of $B_3N_3H_6$.

(10) Burg and Schlesinger, *J. Am. Chem. Soc.*, **59**, 785 (1937)

treated with sodium, one gram equivalent of hydrogen is liberated, per mole of B_2H_7N originally used. After completion of the reaction and removal of excess ammonia, the residue corresponds to the empirical formula $B_2H_7N \cdot NH_2Na$. The significance of these facts is discussed later.

A 5.65-cc. sample of B_2H_7N was dissolved in liquid ammonia at -77° ; the solution was treated with 30 mg. of pure sodium, in the manner described in an earlier paper.¹¹ The resulting evolution of hydrogen was not very rapid, but it finally amounted to one gram equivalent per mole of B_2H_7N , as shown in Table IV.

TABLE IV
REACTION OF $B_2H_7N \cdot NH_3$ WITH SODIUM IN LIQUID AMMONIA

Total time, min.	Temp. during time before meas., $^\circ C$.	Total H evolved, cc.	Ratio of H to B_2H_7N
16	-67	1.55	0.55
32	-55	2.45	.87
57	-60	2.90	1.03
130	-66	3.03	1.07

Reaction beyond that point was exceedingly slow. The major part of the ammonia was removed by distillation at -50° ; a further 0.4 cc. (gas) was lost by the residue during seventy-six hours *in vacuo* at room temperature, conditions so severe that 4.0 cc. of hydrogen also was liberated. The residue was hydrolyzed completely by 3 normal hydrochloric acid; then the excess acid was distilled off and replaced by sodium hydroxide. The ammonia was determined, partly by measurement of the purified gas (9.05 cc.) and partly by titration (1.75 cc.). The total, 10.8 cc., amounts to 1.9 moles of ammonia per mole of B_2H_7N .

The slow production of somewhat more than one equivalent of hydrogen by reaction with sodium in liquid ammonia might well be due to a secondary reaction analogous to that of the "diammoniate of diborane."⁴

Discussion

Only two of the conceivable structures for the compound B_2H_7N seem worthy of serious discussion: (1) an amine of diborane, $B_2H_6NH_2$, and (2) a structure involving a B-N-B skeleton.¹² All derivatives of diborane, not immediately ammonolyzed, take up two molecules of ammonia per molecule of diborane derivative, to form stable compounds. The substance B_2H_7N , however, takes up only one molecule of ammonia; further addition, if it occurs at all, leads to very unstable addition products. This fact is sufficient to exclude further discussion of the first formulation.

The assumption of a B-N-B skeleton leads to

(11) Schlesinger and Burg, *J. Am. Chem. Soc.*, **60**, 293 (1938).

(12) Other ideas are represented by the formulas $NH_4B_2H_4$, $NH_3 \cdot B_2H_4$, $NH_3 \cdot BHBH_3$, and $H^+B_2H_6N^-$. Each of these is difficult to reconcile with some of the physical and chemical properties described in this paper.

two possible structures: (I) BH_3NHBH_3 ¹³ and (II) $BH_2NH_2BH_3$. Formula I not only requires assumptions with regard to electronic distribution, unjustified by any of the chemical properties thus far known for the compound, but fails to explain why one and only one molecule of ammonia can be added to it. When structure II

is represented electronically, $\begin{array}{c} H & H & H \\ & \ddot{B} & : \ddot{N} : \ddot{B} : H \\ & H & H & H \end{array}$, the ad-

dition of one molecule of ammonia (to the one "unsatisfied" boron atom) is understood readily. Compounds in which boron atoms are associated with only six bonding electrons are, of course, very common (*e. g.*, BF_3 , BCl_3 , BR_3 , and their substitution products) and, if not ammonolyzed, take up one molecule of ammonia for each such boron atom present. They are also capable of adding trimethylamine in the same ratio, as does the compound B_2H_7N . On the other hand, compounds containing the BH_3 group tend to give borine trimethylamine, $BH_3 \cdot N(CH_3)_3$, a product which actually is obtained when the addition compound $B_2H_7N \cdot N(CH_3)_3$ is heated with an excess of the amine.

According to structure II, the addition of one mole of ammonia to B_2H_7N results in the com-

pound $\begin{array}{c} H & H & H \\ & \ddot{B} & : \ddot{N} : \ddot{B} : H \\ & H & H & H \end{array}$. This structure is analo-

gous to that of borine ammine (H_3NBH_3) for in each an ammonia molecule is coordinatively bound to a boron atom. Although borine ammine has not been isolated, it has been shown by indirect methods⁴ to react in liquid ammonia solutions with sodium to liberate one gram equivalent of hydrogen for every mole of ammonia bound in that manner. The compound $H_3NB_2H_7N$ reacts to give the same proportion of hydrogen. This cannot mean that the original ammonia addition product was an ammonium salt, for sodium would have reacted with such a salt to remove one nitrogen atom as ammonia, leaving a residue of the composition NaB_2H_6N , instead of the salt $NaNH_2 \cdot B_2H_7N$ actually obtained as a final product.

Other details of the behavior of the compound are in full agreement with formula II. Its stability is characteristic of compounds containing

(13) According to the usual electronic formulations, two possibi-

ties exist for structure I: $\begin{array}{c} H & H & H \\ & \ddot{B} & : \ddot{N} : \ddot{B} : H \\ & H & H & H \end{array}$ and $\begin{array}{c} H & H & H \\ & \ddot{B} & : \ddot{N} : \ddot{B} : H \\ & H & H & H \end{array}$.

Neither of these avoids the difficulties pointed out for the less specific formula I.

a B-N-B pattern of linking, rather than of those containing B-B bonds; the B-N-B skeleton explains why the compound, when heated, gives good yields of $B_3N_3H_6$, a substance containing

the  ring; its rapid hydrolysis in acid solution to give five volumes of hydrogen suggests the existence of five B-H bonds.

Finally, attention is called to a recent paper by S. H. Bauer,¹⁴ who, at the suggestion of Professor Schlesinger and Dr. Burg, investigated the electron diffraction of the vapor of this compound, and concluded that the data obtained can be explained only by the existence of a B-N-B skeleton for the molecule.

Summary

The new volatile compound B_2H_7N (b. p. 76.2° ; m. p. -66.5°) was prepared by the action of diborane upon its "diammoniate." The new substance is hydrolyzed easily in acid solution, to give

(14) S. H. Bauer, *J. Am. Chem. Soc.*, **60**, 524 (1938).

five volumes of hydrogen, two equivalents of boric acid, and one equivalent of ammonium ion. Its thermal decomposition (slow at room temperature) produces diborane and a solid of undetermined character. It reacts with an equal gas volume of trimethylamine, to form a stable white solid; on heating with an excess of that amine, this product yields borine trimethylamine. With ammonia, B_2H_7N forms the stable solid $B_2H_7N \cdot NH_3$, which, on heating to 200° , gives a good yield of triborine triamine ($B_3N_3H_6$). The ammonia addition product reacts with sodium in liquid ammonia to liberate one equivalent of hydrogen; the residue after thorough removal of the solvent corresponds to the formula $NaNH_2 \cdot B_2H_7N$.

H H H

The structure $\begin{array}{c} \ddot{B} : \ddot{N} : \ddot{B} : H \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ is proposed for the

compound, and although this specific picture is not considered definitely proved, it is shown to interpret satisfactorily all of the physical and chemical properties of the substance.

